

UDC 666.3.022:534.8

RHEOLOGICAL CHARACTERISTICS OF THERMOPLASTIC DISPERSE SYSTEMS TREATED WITH ULTRASOUND

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Translated from *Steklo i Keramika*, No. 4, pp. 19–21, April, 2008.

The effect of ultrasound treatment on the rheological behavior of oxide – thermoplastic binder disperse systems was investigated. The possibility of adjusting the characteristics of thermoplastic slips by varying the length of the ultrasound treatment was demonstrated.

The effect of ultrasound vibrations on disperse systems is accompanied by a change in their structure and consequently a change in the rheological properties [1]. In this respect, it is interesting to evaluate the possibility of effectively controlling the process parameters of the thermoplastic slips used for hot molding of ceramic products with ultrasound.

We investigated thermoplastic slips made from H1 beryllium oxide powder with a specific surface area of 1.57 m²/g and a temporary industrial binder of the composition (%³): 82 V2 paraffin, 15 wax, 3 pure-grade oleic acid. The slips were prepared with technology that consisted of mixing the powder with the binder in an impeller reactor for 24 h at 80–85°C. The viscosity and ultimate shear stress were determined with a RV-UZ rotary viscometer (RF Patent No. 59827) with the method in [2].

The effect of the duration of the ultrasound treatment on the viscosity was investigated as a function of the slip temperature (55–74°C) and binder content (9.5–11.7%). The character of flow in the investigated systems was simultaneously analyzed, as there is no published data on this subject. Since the rheological characteristics of the slips are greatly determined by the ratio of the disperse and dispersion media, the change in the volume phase characteristics in casting systems was additionally evaluated in the experiments: critical concentration of solid phase in the system C_v^{cr} and ratios of kinetically free C_ω^{kf} and kinetically bound C_ω^b binder. The relative density of the solid phase in the sediment obtained after 60 min of centrifugation of the slip at 90°C was used as the critical concentration of solid phase in the slip. For this purpose, after cooling, the sediment was sepa-

rated from the binder extruded onto the surface and fired at 1000°C. Based on the size of the ignition losses, the mass content of binder is then determined and this index is recalculated for the volume content of dispersion phase at 75°C with consideration of the change in the binder density as a function of the temperature. Coefficient K_b , which characterizes the ratio of the kinetically free and kinetically bound binder in the slip, was calculated with the equation:

$$K_b = \frac{C_\omega^b}{C_\omega^{kf}} = \frac{C_v(1 - C_v^{cr})}{C_v^{cr} - C_v},$$

where C_v is the volume content of solid phase; $C_v = 1 - \omega\rho_s[(1 - \omega)\rho_b + \omega\rho_s]^{-1}$ (ω is the relative mass content of binder, a fraction; ρ_b and ρ_s are the densities of the binder and solid phase, g/cm³).

The analysis of the experimental data in Table 1 shows that the ratio between the proportions of kinetically free and kinetically bound binder changes with an increase in the ultrasound treatment time in these disperse systems, and this indicates the intensive occurrence of mass exchange processes on the phase boundary. Activation of mass exchange alters the character of flow and the viscosity of thermoplastic slips (Fig. 1, Table 2).

For systems with 10.0% binder, thixotropic (industrially favorable) flow is observed in the region of brief (under 5 min) ultrasound treatments and low temperatures (below 63°C). Increasing the binder content (11.7%) widens the time interval of ultrasound treatment in which the region of thixotropic flow is shifted to the region of higher treatment times and temperatures.

No rigorous mechanisms in the change in the coordinates of the characteristic point of thixotropic-dilatant flow (shear stress and minimum viscosity). Without ultrasound, the values of these parameters are relatively close, but they increase in most cases as the ultrasound treatment time increases,

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³ Here and below: mass content.

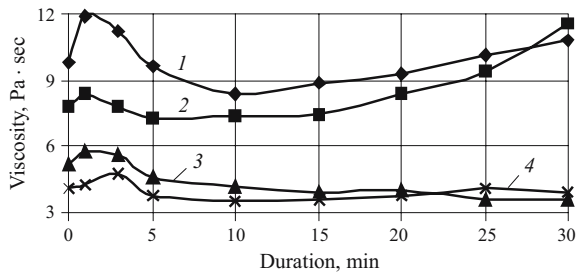


Fig. 1. Viscosity of slips as a function of ultrasound treatment time (3 kW power, 11.7% binder content): 1, 2, 3, and 4) temperature of 59, 63, 68, and 74°C, respectively.

which confirms a single mechanism of structure formation of the slips in the entire range of the variable parameters.

The character of the curve of the viscosity as a function of the duration of ultrasound exposure [$\eta = f(t)$] is not a function of the slip temperature (see Fig. 1) and amount of binder (Fig. 2). A nonmonotonic change in the viscosity as the treatment time increases is a distinctive feature of slips with a different binder content in the investigated temperature range. Two characteristic segments can be distinguished on the curves of the viscosity as a function of the ultrasound treatment time: the first is at a treatment time of less than 5 min and the second is at treatment for more than 5 min. The extremum in the first segment of curve $\eta = f(t)$ (see Fig. 1, $t < 5$ min) is probably due to a change in the granulometric composition of the solid phase in the disperse systems [3]. The driving force of this process is the cavitation that arises in the ultrasound field.

Setting the value of the pressure in the center of a collapsing cavitation bubble within the limits of $10^2 - 10^3$ MPa [4] and also since the center of collapse is not on the surface of a solid particle but some distance from it, we can conclude that the stress applied on the oxide powder particle will be 2–3 orders of magnitude lower than its theoretical strength. In this case, even despite the fact that the strength of oxides is much lower than their theoretical strength ($10^4 - 10^5$ MPa) due to the defectiveness of the structure of the particles, the cavitation burst energy will usually be insufficient to destroy particles with a certain low degree of defectiveness. For this reason, we can hypothesize with sufficient certainty that disaggregation of powder particles bound by autoadhesive forces is the basic process that determines the change in the

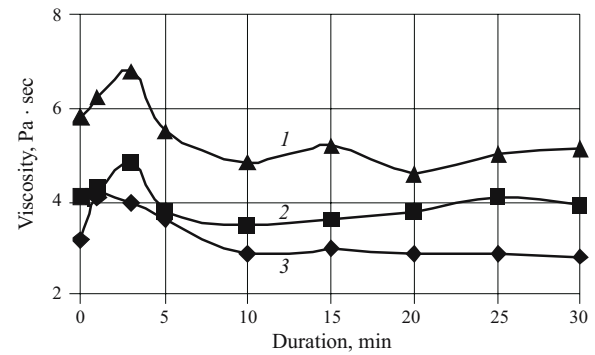


Fig. 2. Viscosity of slips with a binder content of 10.0% (1), 10.7% (2), and 11.7% (3) as a function of ultrasound treatment time (3 kW power, 74°C).

granulometric composition in the investigated range of ultrasound treatment times.

However, not only a cavitation microburst can be the cause of destruction of particles and aggregates. Particles and aggregates of the disperse phase move and collide under the effect of the acoustic flows formed in the liquid and the microjets arising near the cavitation bubble when it collapses. The velocity of the microjets of liquid whose radius corresponds to the minimum radius of the cavitation bubbles is close to the rate of their collapse and attains the sound velocity in the liquid of $(1.5 - 2.0) \times 10^3$ m/sec [3]. The kinetic energy required for destroying aggregates of 0.1, 0.01, and 0.001 μm powder particles during collision and calculated with the method proposed in [4] is from 10 to 10^3 MPa. This is commensurate with the pressure created when a cavitation bubble bursts and consequently the collision factor can also affect destruction of particles and aggregates.

The increase in the viscosity in conditions of brief treatment times (1–5 min) is thus probably due to the formation of “new” surfaces that adsorb the binder, causing it to be redistributed in the bulk of the disperse system. The result of this redistribution is an increase in the proportion of liquid phase in the kinetically bound state in the solvation shells around the particles of solid phase because of a decrease in the amount of kinetically free binder (see Table 2). Due to solvation of some of the dispersion medium, the hydrodynamic volume of the particles increases and the effective volume of disperse phase consequently also increases. Due to

TABLE 1

Binder content, %	C_v	Slip structural parameters with ultrasound treatment time of, * min							
		0		5		15		30	
		C_v^{cr}	K_b	C_v^{cr}	K_b	C_v^{cr}	K_b	C_v^{cr}	K_b
10.0	0.695	0.734	4.6	0.728	5.7	0.730	5.3	0.730	5.3
10.7	0.679	0.728	3.7	0.724	4.2	0.727	3.8	0.727	3.8
11.7	0.657	0.723	2.7	0.720	2.9	0.725	2.6	0.725	2.6

* At 75°C.

TABLE 2

Binder content, %	Temperature, °C	Slip flow characteristics for ultrasound treatment time of					
		0	1	5	10	15	30
10.0	60	T*	T	T	TD 125/65	TD 175/54	T
	63	TD* 210/70**	T	T	TD 150/105	TD 200/110	TD 220/115
	70	D* 150/95	T	TD 170/135	TD 300/380	TD 230/300	TD 270/120
	74	D 170/120	TD 170/115	TD 270/110	—	TD 170/138	TD 280/180
	10.7	60	TD 120/85	TD 130/110	TD 230/130	T 300/145	—
	63	TD 190/80	TD 140/78	TD 160/80	T	TD 130/75	D
11.7	70	TD 120/20	TD 120/30	—	TD 150/78	TD 180/82	—
	59	TD 150/95	T	T	D	D	D
	63	TD 120/70	TD 130/57	TD 110/57	T	T	TD 130/48
	68	TD 150/50	T	T	T	T	T
	74	TD 110/48	TD 80/82	TD 140/82	—	TD 120/80	D 120/117

* T, TD, D) thixotropic, thixotropic-dilatant, and dilatant flow.

** In the numerator: stress, in the denominator: minimum viscosity of thixotropic-dilatant flow.

these events, the viscosity of the slip increases with ultrasound treatment for less than 5 min.

The decrease in the viscosity of the slips with ultrasound treatment longer than 5 min (second segment on the curve of $\eta = f(t)$) is probably due to intensive mass-exchange processes on the dispersion and disperse phase boundary. This mass exchange, induced by the well-known mechanisms of wave processes that take place in disperse systems [1], causes more intensive adsorption of oleic acid and wax on the phase boundary, which improves wetting of the solid phase. This reduces the thickness of the solvation shells, which results in an increase in the proportion of kinetically free binder (see Table 2). Microflows, especially turbulent flows near cavitation bubbles, probably play the greatest role in redistribution of the binder. These flows, formed on the phase boundary, alter the character of the diffusion boundary layer directly adjacent to the surface of the powder particles and improve the wettability of the surface of the disperse phase, which results in formation of a much thinner boundary layer than in natural or forced convection [3].

The slight increase in the viscosity in longer ultrasound treatment (15 – 30 min), primarily observed in “cold” slips (below 63°C) is probably due to dispersion of crystallites of the saturated hydrocarbons that make up the paraffin. This causes a decrease in the proportion of oleic acid and wax components in the boundary layers due to their migration due to dispersion of crystallites of hydrocarbons with a

higher molecular weight. The result of the last process is a decrease in the thickness of the layers of melt that play the role of a lubricant and are in the kinetically free state.

The analysis of the experimental data shows that the change in the viscosity, character of flow, and ratio of kinetically bound and kinetically free binder that occur in exposure to intensive ultrasound is due to a number of specific effects that arise in liquid media under the effect of powerful ultrasound fields. Varying the treatment time allows relatively significantly altering the rheological behavior of thermoplastic slips. We can thus draw a conclusion concerning the effectiveness of controlling the casting properties of disperse system with this process method in formation of ceramics by hot casting using ultrasound.

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